



# Adsorption and catalytic thermolysis of gaseous urea on anatase TiO<sub>2</sub> studied by HPLC analysis, DRIFT spectroscopy and DFT calculations

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## ABSTRACT

High-purity gaseous urea was generated by passing a carrier gas at 100 °C through an inert cordierite monolith impregnated with urea, and the gaseous urea adsorbed onto anatase TiO<sub>2</sub> catalyst samples. Urea adsorption on the catalysts was confirmed by two independent methods: high performance liquid chromatography (HPLC) analysis and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Moreover, urea adsorption at the anatase (1 0 1) surface was studied by density functional theory (DFT) calculations. In combination with the DRIFT spectra, the DFT calculations indicated that two different adsorbed states of deprotonated urea were present on the catalyst simultaneously: in one adsorbed state, urea bound at one Ti site, and in the other adsorbed state urea was rotated and bound at two Ti sites. The confirmation of urea adsorption on anatase supports our previous finding that urea thermolysis is a catalytic reaction.

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## 1. Introduction

In the selective catalytic reduction (SCR) of NO<sub>x</sub> in diesel vehicles, urea solution is dosed into the hot exhaust to produce the actual reducing agent, ammonia [1]. According to the established mechanism, urea first thermolyzes to yield ammonia and isocyanic acid (HNCO) in a non-catalytic reaction, and the intermediately formed HNCO is subsequently hydrolyzed on the SCR catalyst or on a dedicated hydrolysis catalyst [2]. However, a large fraction of the dosed urea remains unreacted before it enters the catalyst [1]. Therefore, the possibility that urea thermolysis is a catalytic reaction should also be considered.

Urea thermolysis :  $\text{CO}(\text{NH}_2)_2 \rightarrow \text{NH}_3 + \text{HNCO}$

HNCO hydrolysis :  $\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2$

In fact, scattered information in the literature indicates that urea thermolysis itself is catalyzed on metal oxide and SCR catalysts [3–6]. Recently, we have reported about catalytic urea thermolysis under steady-state conditions [7,8]. Our results clearly demonstrated the catalytic nature of this reaction, with anatase TiO<sub>2</sub> being

the most active catalyst among those tested. The activities exhibited the order TiO<sub>2</sub> > H-MFI > Al<sub>2</sub>O<sub>3</sub> > ZrO<sub>2</sub> > SiO<sub>2</sub>.

Larrubia et al. have studied the adsorption of urea onto a V<sub>2</sub>O<sub>5</sub>–MoO<sub>3</sub>–TiO<sub>2</sub> SCR catalyst using transmission/absorption Fourier transform infrared spectroscopy [5]. They managed to adsorb gaseous urea on the catalyst surface; however, NH<sub>3</sub> and CO<sub>2</sub> were the main species in the gas phase. Significantly better results were obtained when a mixture of solid urea and catalyst powder was heated under vacuum to remove non-adsorbed bulk urea. As a result of heating, a characteristic peak of bulk urea (1454 cm<sup>−1</sup>) disappeared, which indicated that only adsorbed urea and decomposition products remained in the sample. The spectra of the adsorbed urea showed a strong new band at 1562–1552 cm<sup>−1</sup>, which was attributed to the asymmetric OCN stretching mode of adsorbed urea. Hence, Larrubia et al. proposed that urea adsorbs in its anionic form, as shown in Fig. 1 [5].

In the present study, we recorded diffuse reflectance infrared Fourier transform (DRIFT) spectra of urea adsorbed onto an anatase TiO<sub>2</sub> catalyst. DRIFT samples were prepared via the adsorption of high-purity gaseous urea onto the catalyst. Catalyst samples were washed, and the washing solutions were analyzed using high performance liquid chromatography (HPLC) to independently confirm urea adsorption of the urea. To investigate how urea adsorbs, we performed density functional theory (DFT) calculations of urea adsorbed at the anatase TiO<sub>2</sub> (1 0 1) surface.

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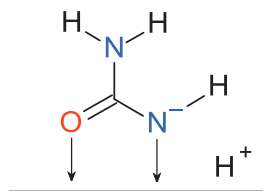


Fig. 1. Adsorbed urea in its anionic form, as proposed by Larrubia et al. [5].

## 2. Experimental and theoretical details

### 2.1. DRIFT samples and catalyst coating

DRIFT samples were prepared via three different methods:

- Adsorption of gaseous urea onto anatase  $\text{TiO}_2$  catalyst powder (Crystal Global DT-51), see Section 2.2. Abbreviation: “urea (g)”. Additionally,  $\text{NH}_3$  was adsorbed onto  $\text{TiO}_2$ . Before adsorbing  $\text{NH}_3$ , the  $\text{TiO}_2$  sample was cleaned at  $450^\circ\text{C}$  inside the DRIFT cell, then the temperature was set to  $60^\circ\text{C}$  and the DRIFT cell was supplied with 200 ppm  $\text{NH}_3$  in  $\text{N}_2$  for 75 min.
- Mixing of urea solution with catalyst powder by sonication for 3 min, followed by drying under ambient conditions. Abbreviation: “urea (aq)”. For comparison,  $\text{TiO}_2$  samples with biuret, cyanuric acid, ammeline and melamine were prepared likewise. Ammelide was suspended at 0.1% concentration.
- Dry grinding of solid urea (Merck,  $\geq 99.5\%$  purity) with catalyst powder,  $\text{CaF}_2$  (Sigma–Aldrich, puriss.),  $\text{KBr}$  (Fluka,  $>99\%$  purity) or cordierite (Corning). Abbreviation: “urea (s)”.

The BET surface area of the anatase  $\text{TiO}_2$  catalyst was  $90\text{ m}^2/\text{g}$ , measured on a Quantachrome Autosorb 1-c instrument under relative pressures  $p/p_0$  that ranged from 0.05 to 0.3. The particle size was  $\text{ØD50} = 1.70\text{ }\mu\text{m}$ , measured on a Horiba LA-950 laser diffraction particle analyzer [9].

In addition to catalyst powder, gaseous urea was also adsorbed onto a  $\text{TiO}_2$ -coated cordierite monolith, which was prepared as described previously [9]. The monolith was coated with 0.6 g of  $\text{TiO}_2$  (including 10% wt% commercial silicate binder, Ludox AS-40).

### 2.2. Adsorption and thermolysis of gaseous urea onto $\text{TiO}_2$

Gaseous urea was obtained by passing a carrier gas at  $100^\circ\text{C}$  and at atmospheric pressure through an inert cordierite monolith that was impregnated with urea. According to our previous study, urea desorbed from the monolith in monomolecular form [10]. The applied temperature of  $100^\circ\text{C}$  was expected to result in a urea concentration of 27 ppm in the gas phase (assuming saturation) [10,11]. Because of the low temperature applied, non-catalytic urea decomposition was negligible [10].

To perform urea adsorption, a sample of  $\text{TiO}_2$ -catalyst powder was charged into a crucible and placed in the hot urea-containing carrier gas, as shown in Fig. 2. Because the  $\text{TiO}_2$  catalyst was also exposed to the sublimation temperature of  $100^\circ\text{C}$ , urea had to adsorb onto the catalyst rather than condense into the

bulk form. Notably, at the reactor exit, where the temperature was lower, the urea vapor condensed and formed needle-shaped crystals.

Urea adsorption was performed in a tubular quartz reactor with an inner diameter of 28 mm. The setup has been described in detail elsewhere [10]. An inert cordierite monolith (400 cpsi, 40 mm long, 17.5 mm wide and 12.4 mm high) was impregnated with 430 mg of urea by dipping it into 40 wt% urea solution. The impregnated monolith was inserted into a metal adaptor and the metal adaptor was placed in the reactor. The  $\text{N}_2$  carrier gas flow was set to 200 L/h at standard temperature and pressure (STP), which resulted in a GHSV of  $23,000\text{ h}^{-1}$  through the impregnated monolith. The impregnated monolith was first dried inside the reactor at  $70^\circ\text{C}$ , and the crucible with  $\approx 0.1\text{ g}$  of  $\text{TiO}_2$  was subsequently placed in the metal adaptor, as shown in Fig. 2. In some of the experiments, a humid gas mixture composed of 3%  $\text{H}_2\text{O}$ , 10%  $\text{O}_2$  and balance  $\text{N}_2$  was used as the carrier gas instead of pure  $\text{N}_2$ . Because drying of the impregnated monolith catalyst was not necessary in this case, the catalyst powder was placed in the reactor at the beginning.

In addition, we performed urea adsorption at  $100^\circ\text{C}$  and urea thermolysis at  $130^\circ\text{C}$  on  $\text{TiO}_2$ -coated monoliths (20 mm long, other dimensions identical to those of the inert monolith) inserted into the metal adaptor instead of the crucible. Urea thermolysis on the  $\text{TiO}_2$ -coated monolith was performed with a flow of 10%  $\text{O}_2$  in  $\text{N}_2$  at a rate of 431 L/h at STP (GHSV =  $98,000\text{ h}^{-1}$ ).

### 2.3. HPLC analysis

To quantify the adsorbed urea and the eventual urea decomposition byproducts on the  $\text{TiO}_2$  samples, we applied HPLC analysis using a Dionex UltiMate 3000 instrument equipped with an anion exchange column (Waters WAT026770 IC-PAK ANION HC  $4.6 \times 150$ ) and a photodiode-array detector. A 5 mM sodium phosphate buffer solution adjusted to pH 10.4 was used as the eluent, which allowed the separation of the most important urea decomposition byproducts [10]. The UV absorption was measured at 5 wavelengths simultaneously: 192 nm for urea, 204 nm for melamine, 214 nm for cyanuric acid, 230 nm for ammeline and 197 nm for biuret and most of the other compounds. Liquid samples were obtained by washing a monolith or a sample of catalyst powder in the HPLC eluent overnight [9].

For the urea thermolysis experiment conducted at  $130^\circ\text{C}$ , gaseous urea and  $\text{HNCO}$  were absorbed out of the carrier gas by a liquid-quench probe [12,13] and then quantified by HPLC. Three liquid samples were collected sequentially at intervals of 5 min. The results are given in the form “average  $\pm$  standard deviation”.

### 2.4. DRIFT measurements

DRIFT spectra were measured on a ThermoNicolet Nexus FTIR spectrometer at a resolution of  $4\text{ cm}^{-1}$  using the Smart Collector and Environmental Chamber accessories. The Environmental Chamber is a heated DRIFT cell that is equipped with ZnSe windows and gas supply lines. The samples were placed in the sample holder and pressed and flattened with a spatula. The DRIFT cell was always purged with either pure  $\text{N}_2$  (140 L/h at STP) or with a gas mixture composed of 3% water, 10%  $\text{O}_2$  and balance  $\text{N}_2$  (200 L/h at STP).

DRIFT spectra were measured at various temperatures up to  $300^\circ\text{C}$ . The measurements were started at low temperature, and the temperature was increased step-wise. All of the shown spectra are subtraction spectra. Background spectra of urea-free samples were recorded under dry  $\text{N}_2$  at the same temperatures as the actual samples.

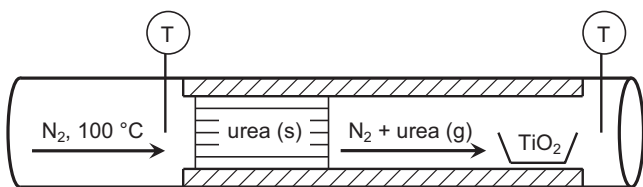


Fig. 2. Schematic of the experimental setup for urea evaporation and adsorption onto  $\text{TiO}_2$ .

**Table 1**  
HPLC analysis of catalyst and monolith washing solutions.

| Sample                    | Carrier gas         | Duration (h) | Urea/TiO <sub>2</sub> (wt%) | Composition of compounds in washing solution, (wt%) |        |         |      |           |       |
|---------------------------|---------------------|--------------|-----------------------------|---|--------|---------|------|-----------|-------|
|                           |                     |              |                             | Urea  | Biuret | Triuret | HNCO | Cyanamide | CYA   |
| TiO <sub>2</sub> powder   | Dry N <sub>2</sub>  | 21.5         | >1                          | 94.0  | 5.9    | 0.1     | 0    | 0         | 0     |
| TiO <sub>2</sub> monolith | Dry N <sub>2</sub>  | 20.5         | 4.3                         | 73.9  | 21.7   | 1.5     | 1.8  | 0.69      | 0.18  |
| TiO <sub>2</sub> monolith | 3% H <sub>2</sub> O | 18           | 5.5                         | 99.5  | 0.5    | 0       | 0    | 0         | 0.003 |
| Inert monolith            | Dry N <sub>2</sub>  | 21.5         | 110 mg                      | 99.99   | 0      | 0.005   | 0    | 0         | 0.002 |

## 2.5. Computational details

The electronic structure of the Ti<sub>8</sub>O<sub>28</sub>H<sub>24</sub> cluster, which represents the (1 0 1) surface of anatase, and that of the urea adsorbates was calculated using ab initio DFT methods (StoBe code [14]). We chose to consider the (1 0 1) surface because it was found to be abundant based on high-resolution powder X-ray diffraction results (XRD) in another study [15]. The generalized gradient-corrected functionals according to Perdew, Burke and Ernzerhof (RPBE) were used to account for electron exchange and correlation [16,17]. All Kohn–Sham orbitals were represented by linear combinations of atomic orbitals (LCAOs) with Gaussian basis sets for the atoms [18,19]. The vibration frequencies were calculated by single-point energy calculations of the optimized geometries. The calculations of the vibrational frequencies were performed with harmonic approximations as well as with an anharmonicity fit in the Morse potential function, as implemented in the StoBe code [20].

## 3. Results and discussion

### 3.1. Confirmation of urea adsorption by HPLC analysis

Gaseous urea was adsorbed onto TiO<sub>2</sub> at 100 °C, as described in Section 2.2. Non-catalytic urea decomposition was negligible at 100 °C [10]; however, urea may have decomposed on the catalyst. To confirm that urea was present on the TiO<sub>2</sub> powder samples and to determine whether byproducts were formed, we performed HPLC analysis of catalyst washing solutions. After the adsorption of urea onto TiO<sub>2</sub> powder, part of the sample was used for DRIFT measurements. The remaining sample was washed in the aqueous HPLC eluent, and the washing solution was analyzed by HPLC. In addition, TiO<sub>2</sub>-coated monoliths with adsorbed urea were analyzed likewise. Finally, the inert cordierite monolith that had been impregnated with urea and used as a source of urea vapor was analyzed after the experiment. Table 1 shows the results.

HPLC analysis of the catalyst washing solutions showed that urea was the main (water-soluble) constituent in all the TiO<sub>2</sub> samples. On the TiO<sub>2</sub> powder placed in the crucible and exposed under dry N<sub>2</sub>, we found slightly more than 1 wt% of urea per TiO<sub>2</sub>. In addition to 94% urea, 6% biuret was found in the washing solution. Apparently, some urea was catalytically thermolyzed on the TiO<sub>2</sub> surface to form HNCO, and the HNCO then reacted with intact urea to form biuret [3,9,21]. When a TiO<sub>2</sub>-coated monolith was placed in the reactor instead of a crucible, more urea adsorbed onto the catalyst and more biuret (22%) was formed. Adsorption worked more efficiently on the monolith due to its significantly greater geometric surface area. The resulting greater surface coverage of urea on the TiO<sub>2</sub>-coated monolith may explain the

increased biuret yield compared to that obtained with the powder. Because of its low vapor pressure [9], biuret was accumulated on the catalyst surface during the complete exposure time at 100 °C. In contrast to biuret, very little cyanuric acid was formed. We reported analogous results elsewhere [9], where we concluded that HNCO preferentially combines with urea rather than with biuret. Thermolysis produced significant amounts of cyanuric acid only when a catalyst-coated monolith was impregnated with biuret [9].

When urea was adsorbed from humid carrier gas, very little biuret was formed. In this case, HNCO hydrolyzed due to the presence of water instead of being consumed for biuret formation, or the formed biuret was hydrolyzed again [3,6,9,22,23]. Notably, the urea concentration of approximately 27 ppm was significantly lower than the water concentration of 30,000 ppm, and the catalyst still adsorbed a significant amount of urea. The adsorption of urea from the humid carrier gas indicated that urea adsorbs more strongly onto TiO<sub>2</sub> than does water.

Pure urea was found on the impregnated inert monolith that had been used as the source of urea vapor, which indicated that urea was stable at 100 °C in the absence of a catalyst. Of the initial amount of 430 mg urea, 110 mg remained on the monolith after it had been heated to 100 °C for 21.5 h. Hence, 430 mg – 110 mg = 320 mg urea had evaporated during the experiment. Based on the vapor pressure of urea [10,11], 310 mg of urea was expected to evaporate, which is in good agreement with the measured amount of remaining urea.

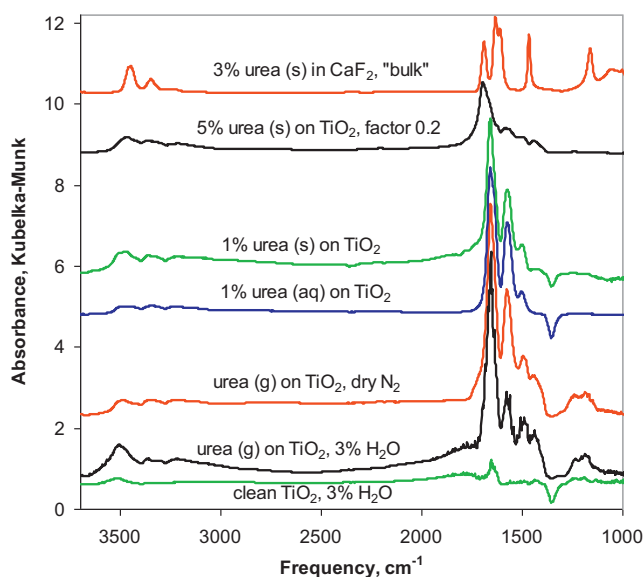
### 3.2. Quasi-stationary thermolysis of gaseous urea on a TiO<sub>2</sub>-coated monolith

Quasi-stationary urea thermolysis over TiO<sub>2</sub> was performed at 130 °C using an impregnated inert monolith as the source of gaseous urea. Instead of the crucible shown in Fig. 2, a TiO<sub>2</sub>-coated monolith was placed in the reactor downstream of the inert monolith. After approximately 30 min of equilibration at 130 °C, three liquid samples with absorbed product gas were collected during 3 × 5 min for HPLC analysis. For comparison, an analogous experiment was performed without a catalyst. Because of the catalytic activity of TiO<sub>2</sub>, the HNCO yield increased from 5% to 35% (Table 2). The carbon balance in both cases agreed fairly well, which indicated that the catalyst was under stationary conditions.

Table 2 shows the results of solvent-free, catalytic thermolysis of gaseous urea. These results support our previous findings about catalytic urea thermolysis under steady-state conditions at various temperatures over different metal oxide catalysts [7,8]. As we have previously reported [7,8], urea was dosed in a borosilicate glass reactor in the form of a water-free organic solution by a gas-assisted spray nozzle. The spray aerosols appeared to evaporate upstream of the catalyst; however, the existence of urea aerosols at the catalyst

**Table 2**  
Quasi-stationary decomposition of gaseous urea at 130 °C. Carrier gas: 10% O<sub>2</sub> in N<sub>2</sub>, 431 L/h at STP.

| 1st monolith (GHSV, h <sup>-1</sup> ) | 2nd monolith (GHSV, h <sup>-1</sup> ) | Urea (ppm) | HNCO (ppm) | Total carbon (ppm) |
|---------------------------------------|---------------------------------------|------------|------------|--------------------|
| Inert (50,000)                        | TiO <sub>2</sub> -coated (98,000)     | 119 ± 0.5  | 63 ± 2     | 181                |
| Inert (50,000)                        | None                                  | 182 ± 9    | 8.6 ± 0.7  | 190                |



**Fig. 3.** DRIFT spectra of urea recorded at 80 °C; the intensities of the “5% urea (s) on TiO<sub>2</sub>” sample were multiplied by a factor of 0.2. Sample preparation methods: urea (g) = urea vapor adsorbed onto catalyst powder at 100 °C; urea (aq) = aqueous urea solution mixed with catalyst powder by sonication, followed by drying under ambient conditions; urea (s) = solid urea mixed with catalyst powder by dry grinding.

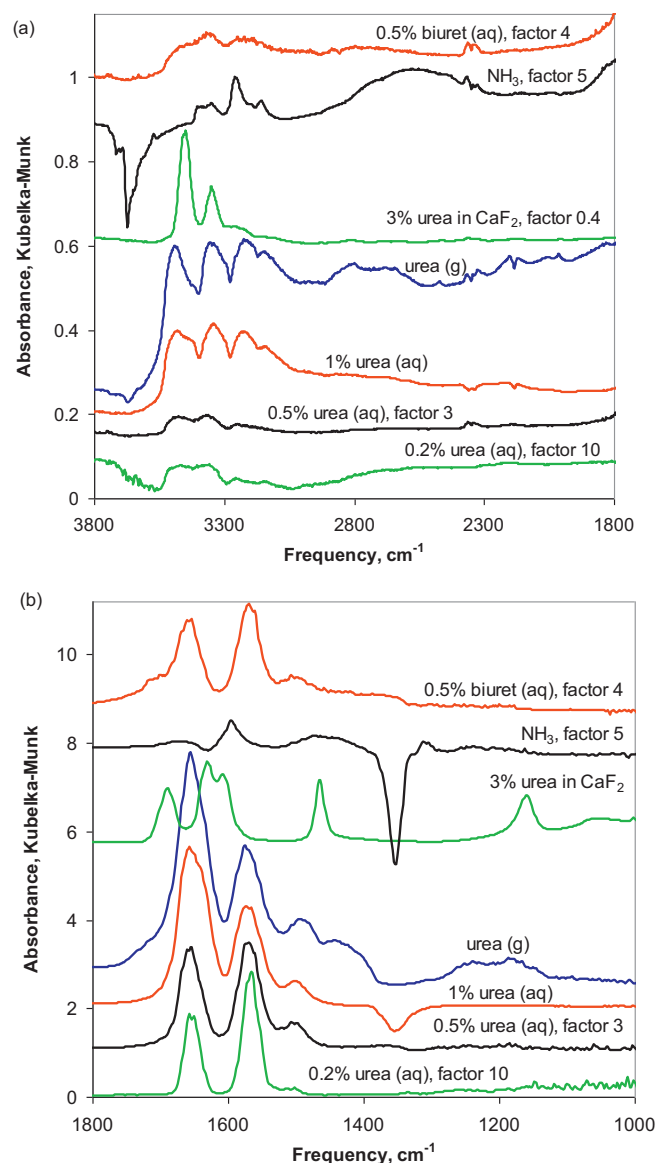
entrance could not be excluded with certainty [7,8]. Additionally, a solvent was always used to dose the urea.

### 3.3. DRIFT measurements at 80 °C

Fig. 3 shows the DRIFT spectra of urea on TiO<sub>2</sub> recorded at 80 °C. A temperature of 80 °C was chosen to desorb weakly adsorbed water without inducing urea decomposition. The spectrum of urea in CaF<sub>2</sub> and that of clean TiO<sub>2</sub> under humid gas are shown for comparison. The latter spectrum was the “ads. urea on TiO<sub>2</sub>” sample after in situ cleaning by hydrolysis at 450 °C. The bottom two spectra in Fig. 3 were recorded under humid model gas; all the other spectra were recorded under dry N<sub>2</sub>. The spectrum of urea in CaF<sub>2</sub> best represented bulk solid urea because it showed better-defined peaks compared to the spectra of urea in KBr or urea in cordierite powder (not shown). Furthermore, our spectrum of urea in CaF<sub>2</sub> agrees best with the spectrum of pure crystalline urea measured by Grdadolnik and Maréchal, who used attenuated total reflectance (ATR) spectroscopy [24].

We attributed the bands of our 3% urea in CaF<sub>2</sub> spectrum using the assignments of Grdadolnik and Maréchal [24], see Table 3. In their study, the absorption bands were assigned based on a comparison of the spectra from different isotopomers of urea (urea with D and/or <sup>13</sup>C) [24]. Here, the bands at 1689 cm<sup>-1</sup> and 1631 cm<sup>-1</sup> were attributed to the NH<sub>2</sub> bending vibrations, the band at 1608 cm<sup>-1</sup> was attributed to the C=O stretching vibration, the band at 1465 cm<sup>-1</sup> was attributed to the CN stretching vibration, and the band at 1160 cm<sup>-1</sup> was attributed to the NH<sub>2</sub> rocking vibration (Table 3).

The spectra of adsorbed urea strongly differed from that of the bulk urea spectrum (see 1% urea (s) on TiO<sub>2</sub>, 1% urea (aq) on TiO<sub>2</sub>, urea (g) on TiO<sub>2</sub> vs. bulk urea in Fig. 3). In the 1% urea (aq) on TiO<sub>2</sub> spectrum, the two prominent peaks of bulk urea at 1465 cm<sup>-1</sup> (CN stretching vibration) and at 1160 cm<sup>-1</sup> (NH<sub>2</sub> rocking vibration) disappeared. On the other hand, new and/or shifted peaks appeared at 1657 cm<sup>-1</sup>, 1573 cm<sup>-1</sup> and 1501 cm<sup>-1</sup>. This change in the urea spectrum is in good agreement with the results reported by Larrubia et al. [5]. The peak assignment of adsorbed urea is discussed in the next section.



**Fig. 4.** DRIFT spectra of different urea on TiO<sub>2</sub> samples, of biuret on TiO<sub>2</sub> and of NH<sub>3</sub> on TiO<sub>2</sub>. All spectra were recorded at 80 °C. NH<sub>3</sub> was adsorbed onto TiO<sub>2</sub> by supplying the DRIFT cell with 200 ppm NH<sub>3</sub> in N<sub>2</sub> at 60 °C for 75 min. The shown NH<sub>3</sub> on TiO<sub>2</sub> spectrum was recorded at 80 °C, 20 min after switching to purging with pure N<sub>2</sub>.

Interestingly, the three different preparation methods for the urea on TiO<sub>2</sub> samples resulted in quite similar spectra (see 1% urea (s) on TiO<sub>2</sub>, 1% urea (aq) on TiO<sub>2</sub> and urea (g) on TiO<sub>2</sub> in Fig. 3). Apparently, urea (aq) predominantly adsorbed onto the same sites of TiO<sub>2</sub> as did gaseous urea. Also, the grinding of solid urea with the catalyst seemed to provide sufficient energy to induce urea diffusion to the same energetically favored adsorption sites of TiO<sub>2</sub>. However, a clearly different spectrum was obtained when 5 wt% instead of 1 wt% of urea was ground with TiO<sub>2</sub>: the 5% urea (s) on TiO<sub>2</sub> spectrum appeared to be a transition from the spectrum of 1% urea on TiO<sub>2</sub> to that of bulk urea. The most intense peak in the spectrum of 5% urea (s) on TiO<sub>2</sub> was located at 1695 cm<sup>-1</sup>, which matches well with the peak at 1689 cm<sup>-1</sup> (NH<sub>2</sub> bending vibration) in the spectrum of bulk urea. The spectrum of 5% urea (s) on TiO<sub>2</sub> did not show other prominent peaks at wavenumbers less than 1800 cm<sup>-1</sup>, but the two most intense peaks in the spectrum of the 1% urea (aq) on TiO<sub>2</sub> at 1655 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> seemed to be present as shoulders in the spectrum of 5% urea (s) on TiO<sub>2</sub>. The



**Table 3**  
Comparison of the vibration frequencies [ $\text{cm}^{-1}$ ] of urea in different samples with the DFT-calculated results (represented in italics) obtained in the present work (p.w.) or with results taken from the literature.

| Urea sample                              | $\nu \text{ NH}_2$  | $\delta \text{ NH}_2$   | $\nu \text{ CO}$  | $\nu_{\text{as}} \text{ Ti—OCN—Ti}$ | $\delta \text{ HN—C—NH}$ | $\nu \text{ CN}$ | $\rho \text{ NH}_2$ | $\delta \text{ NH}$ | Method, source |
|--|---|-------------------------|-------------------|-------------------------------------|--------------------------|------------------|---------------------|---------------------|----------------|
| 3% urea (s) in $\text{CaF}_2$ , 80 °C    | 3447, 3349  | 1689, 1631 <sup>a</sup> | 1608              |                                     |                          | 1465, 1008       | 1160, 1051          |                     | DRIFT, p.w.    |
| Crystalline urea                         | 3437 <sup>a</sup> , 3343                                    | 1682, 1624              | 1599              |                                     |                          | 1466, 1003       | 1156, 1057          |                     | ATR [24]       |
| Adsorbed urea form A                     | 3603, 3479, 3465  | 1638 <sup>a</sup>       |                   | 1578                                | 1438                     | 1002             | 1102                | 1198                | DFT, p.w.      |
| Adsorbed urea form B                     | 3565, 3523 ( $\text{NH}_2$ ),<br>3423, 3393 ( $\text{NH}$ ) | 1638                    |                   | 1579                                | 1375 <sup>a</sup>        | 966              | 1091                | 1221                | DFT, p.w.      |
| Urea (g) on $\text{TiO}_2$ , 80 °C       | 3488, 3353, 3224  | (1635)                  | 1655 <sup>a</sup> | 1575 (1567),<br>(1560)              | 1492, 1443               | 1240             | 1185                | 1240                | DRIFT, p.w.    |
| 1% urea (aq) on $\text{TiO}_2$ , 80 °C   | 3480, 3341, 3231  | (1637)                  | 1657 <sup>a</sup> | 1573 (1566),<br>(1556)              | 1501                     |                  |                     |                     | DRIFT, p.w.    |
| 0.5% urea (aq) on $\text{TiO}_2$ , 80 °C | 3469, 3355, 3250  | (1638)                  | 1654              | 1569 <sup>a</sup> (1560)            | 1506                     |                  |                     |                     | DRIFT, p.w.    |
| 0.2% urea (aq) on $\text{TiO}_2$ , 80 °C |   |                         | 1657 (1651)       | 1566 <sup>a</sup> , (1556)          | 1502                     |                  |                     |                     | DRIFT, p.w.    |
| 0.1% urea (aq) on $\text{TiO}_2$ , 80 °C |   |                         | 1653              | 1568 <sup>a</sup>                   | 1507                     |                  |                     |                     | DRIFT, p.w.    |
| 1% urea (aq) on V-Mo- $\text{TiO}_2$     | 3469, 3365, 3250  |                         | 1652 <sup>a</sup> | 1562–1552                           |                          |                  |                     |                     | FTIR [5]       |
| Gaseous urea                             | 3584–3455   | 1624                    | 1752 <sup>a</sup> |                                     |                          | 1372             |                     |                     | DFT [10]       |
| Gaseous urea                             | 3540, 3437  | 1600                    | 1773 <sup>a</sup> |                                     |                          | 1392             |                     |                     | FTIR [10]      |

In brackets: shoulder.

<sup>a</sup> Most intensive peak.

spectrum of 5% urea (s) on  $\text{TiO}_2$  may be explained by the relatively high surface coverage.

The presence of water in the purge gas of the DRIFT cell (urea (g) on  $\text{TiO}_2$ , 3%  $\text{H}_2\text{O}$  in Fig. 3) caused the superposition of the urea spectrum with numerous small, narrow water signals. Apart from the small water signals, the urea spectrum did not appear to be influenced by the presence of water in the purge gas. We attempted to correct the urea spectrum by subtracting the spectrum of clean  $\text{TiO}_2$  acquired under humid model gas but did not obtain a satisfactory result. Nonetheless, the humid purge gas substantially influenced the spectra when the temperature was increased greater than 100 °C because the NCO band at  $2200 \text{ cm}^{-1}$  was suppressed by HNCO hydrolysis.

Although the spectra of urea (g) on  $\text{TiO}_2$  and 1% urea (aq) on  $\text{TiO}_2$  in Fig. 3 were quite similar, a closer look reveals some differences, see also Fig. 4. The spectrum of urea (g) showed small peaks at  $1443 \text{ cm}^{-1}$ ,  $1240 \text{ cm}^{-1}$  and  $1185 \text{ cm}^{-1}$ , which were not observed in the urea (aq) samples (Fig. 4b). Since the urea (g) on  $\text{TiO}_2$  sample was contaminated with biuret that had formed during urea adsorption at 100 °C (see Table 1), the additional peaks in urea (g) might be attributed to biuret. Also,  $\text{NH}_3$ , which was not quantified by our HPLC method, may have contributed to the urea (g) on  $\text{TiO}_2$  spectrum. However, the 0.5% biuret (aq) and the  $\text{NH}_3$  on  $\text{TiO}_2$  spectra (top two curves in Fig. 4b), did not show peaks at  $1443 \text{ cm}^{-1}$ ,  $1240 \text{ cm}^{-1}$  or  $1185 \text{ cm}^{-1}$ , indicating that these peaks were attributed to adsorbed urea. We assume that the urea distribution on the catalyst surface was more uniform in the urea (g) on  $\text{TiO}_2$  sample than in the urea (aq) on  $\text{TiO}_2$  samples, which allowed the observation of additional peaks.

The negative peak at  $1354 \text{ m}^{-1}$  in the  $\text{NH}_3$  on  $\text{TiO}_2$  spectrum in Fig. 4b was attributed to a breaking of Ti—O—S bonds upon interaction with  $\text{NH}_3$ . Hauck et al. observed a similar negative peak at  $1371 \text{ cm}^{-1}$  [22]. Sulfate species are present in commercial  $\text{TiO}_2$  because of its synthesis via the sulfate method, and the sulfate species show a characteristic band in this region due to their S=O stretching vibration [22]. Our 1% urea (aq) on  $\text{TiO}_2$  spectrum in Fig. 4b and in Fig. 3 also showed a negative peak at the same position, but that peak was smaller.

Fig. 4 also compares urea (aq) on  $\text{TiO}_2$  samples with different urea concentrations. Decreasing the urea concentration changed the relative intensities of the peaks. (At 1% urea concentration, the peak at  $1657 \text{ cm}^{-1}$  was most intense, but at lower concentrations of 0.5%, 0.2% and 0.1% (0.1% not shown), the peak at  $1569 \text{ cm}^{-1}$  became most intense). Further, the relative intensity of the peak at  $1501 \text{ cm}^{-1}$  (compared to the most intense peak) decreased at

low urea concentrations. Anyway, the peaks of urea (g) on  $\text{TiO}_2$  at  $1443 \text{ cm}^{-1}$ ,  $1240 \text{ cm}^{-1}$  and  $1185 \text{ cm}^{-1}$  were not observed in any of the urea (aq) on  $\text{TiO}_2$  samples.

### 3.4. Comparison of DRIFT measurements with DFT calculations

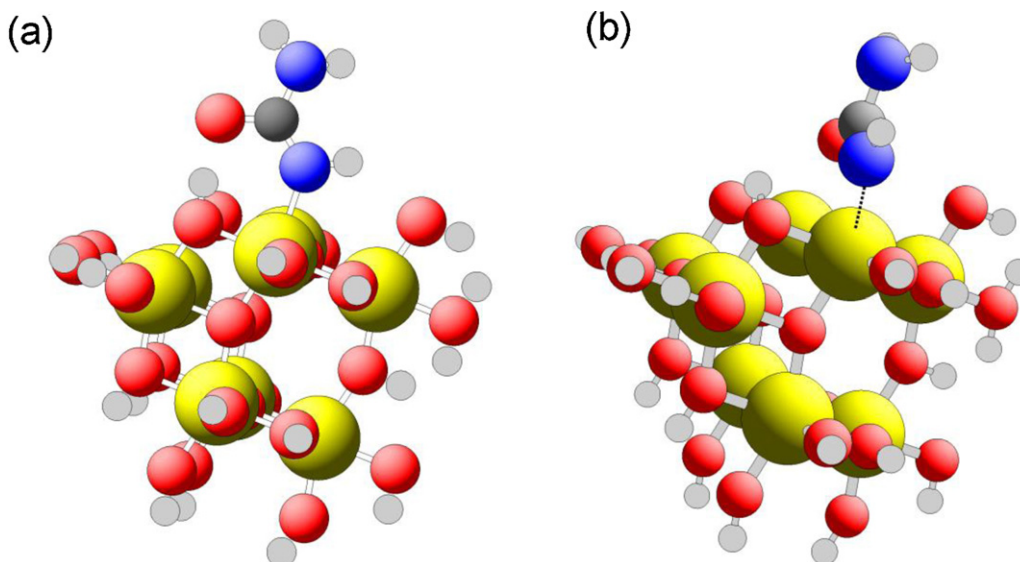
Table 3 shows a comparison of the vibration frequencies of urea in different samples, and the DFT-calculated frequencies. The  $\text{TiO}_2$  cluster with adsorbed urea, shown in Fig. 5, was used for the DFT calculations.

Fig. 5 shows the two different adsorption positions of urea at the anatase  $\text{TiO}_2$  (1 0 1) surface that were found to be most likely. Adsorbed urea A (Fig. 5a) was deprotonated to the anionic form,  $\text{HN}^-\text{C}(\text{O})\text{NH}_2$ , by proton transfer to surface O(2), and bound with the  $\text{HN}^-$  group at one Ti site with an adsorption energy of  $-0.26 \text{ eV}$ . Adsorbed urea B (Fig. 5b) was similarly deprotonated and bound at two Ti sites with both the  $\text{HN}^-$  group and the double-bonded O, with an adsorption energy of  $-0.28 \text{ eV}$ . Notably, adsorbed urea B corresponds to the scheme of adsorption proposed by Larrubia et al. [5]. We also considered zwitterionic urea,  $\text{H}_2\text{NC}(\text{O}^+\text{H})\text{N}^-\text{H}$ , bound with the  $\text{HN}^-$  group at one Ti site with an adsorption energy of  $-0.78 \text{ eV}$ . However, the zwitterionic form should have shown a strong OH stretching vibration band at  $2539 \text{ cm}^{-1}$ , which was not observed in the DRIFT spectra.

Fig. 6 shows a comparison between the experimental DRIFT spectra of urea adsorbed onto  $\text{TiO}_2$  (with urea added in aqueous form in Fig. 6a and with urea in gaseous form in Fig. 6b) and the DFT-calculated frequencies. Fig. 6 focuses on the region below  $1800 \text{ cm}^{-1}$ , because both the experimental and the theoretical spectra showed only peaks with low intensity at higher wavenumbers. Comparison of the urea (g) on  $\text{TiO}_2$  spectrum with the DFT-calculated spectra (Fig. 6b) indicates that the two different adsorbed states of urea shown in Fig. 5 exist on  $\text{TiO}_2$  simultaneously. The two most intense peaks in the experimental spectra are in good agreement with the DFT calculations.

A closer examination of the most intense peak in Fig. 6b at  $1655 \text{ cm}^{-1}$  reveals a shoulder at approximately  $1635 \text{ cm}^{-1}$ , which indicates two overlapping peaks. Based on the calculated intensities, we attributed the main peak to the  $\text{NH}_2$  bending mode of adsorbed urea A (measured:  $1655 \text{ cm}^{-1}$ , calculated:  $1638 \text{ cm}^{-1}$ ) and the shoulder to the  $\text{NH}_2$  bending mode of adsorbed urea B (measured:  $1635 \text{ cm}^{-1}$ , calculated:  $1638 \text{ cm}^{-1}$ ).

The second-most intense peak was measured at  $1575 \text{ cm}^{-1}$ . This peak was attributed to the asymmetric Ti—OCN—Ti stretching modes of adsorbed urea A and B, which were calculated to occur



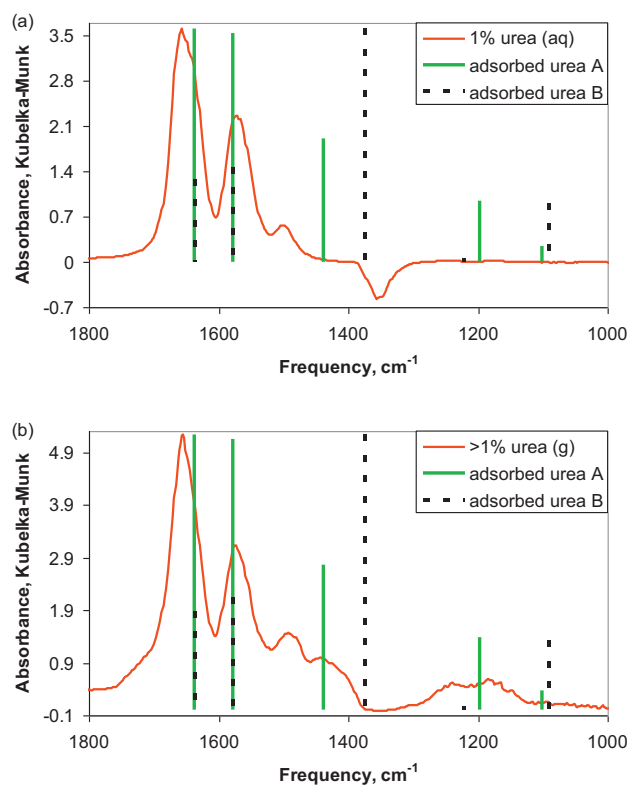
**Fig. 5.** Urea adsorbed onto the  $\text{Ti}_8\text{O}_{28}\text{H}_{24}$  cluster, which represents the (101)  $\text{TiO}_2$  surface; these results were used for the DFT calculations; (a): adsorbed urea form A; (b): adsorbed urea form B.

at  $1578\text{ cm}^{-1}$  and  $1579\text{ cm}^{-1}$ , respectively. Larrubia et al. observed a similar peak in the spectrum of urea on a  $\text{V}_2\text{O}_5\text{--MoO}_3\text{--TiO}_2$  SCR catalyst at  $1562\text{--}1552\text{ cm}^{-1}$ , which they considered to be characteristic for adsorbed urea [5]. They also assigned their peak at  $1562\text{--}1552\text{ cm}^{-1}$  to the asymmetric  $\text{Ti--OCN--Ti}$  stretching mode [5].

The next most intense peaks in the urea (g) on  $\text{TiO}_2$  spectrum (Fig. 6b) were measured at  $1492\text{ cm}^{-1}$  and  $1443\text{ cm}^{-1}$ . These peaks were attributed to the  $\text{HN--C--NH}$  scissoring modes of adsorbed

urea A (measured:  $1492\text{ cm}^{-1}$ , calculated:  $1438\text{ cm}^{-1}$ ) and of adsorbed urea B (measured:  $1443\text{ cm}^{-1}$ , calculated:  $1375\text{ cm}^{-1}$ ). Further, the small peak at  $1240\text{ cm}^{-1}$  was attributed to a combination of the  $\text{NH}$  bending of adsorbed urea A at  $1198\text{ cm}^{-1}$  and to the  $\text{CN}$  stretching mode of adsorbed urea B at  $1221\text{ cm}^{-1}$ . The nearby peak at  $1185\text{ cm}^{-1}$  was assigned to the  $\text{NH}_2$  rocking modes of adsorbed urea A and B at  $1102\text{ cm}^{-1}$  and  $1091\text{ cm}^{-1}$ , respectively.

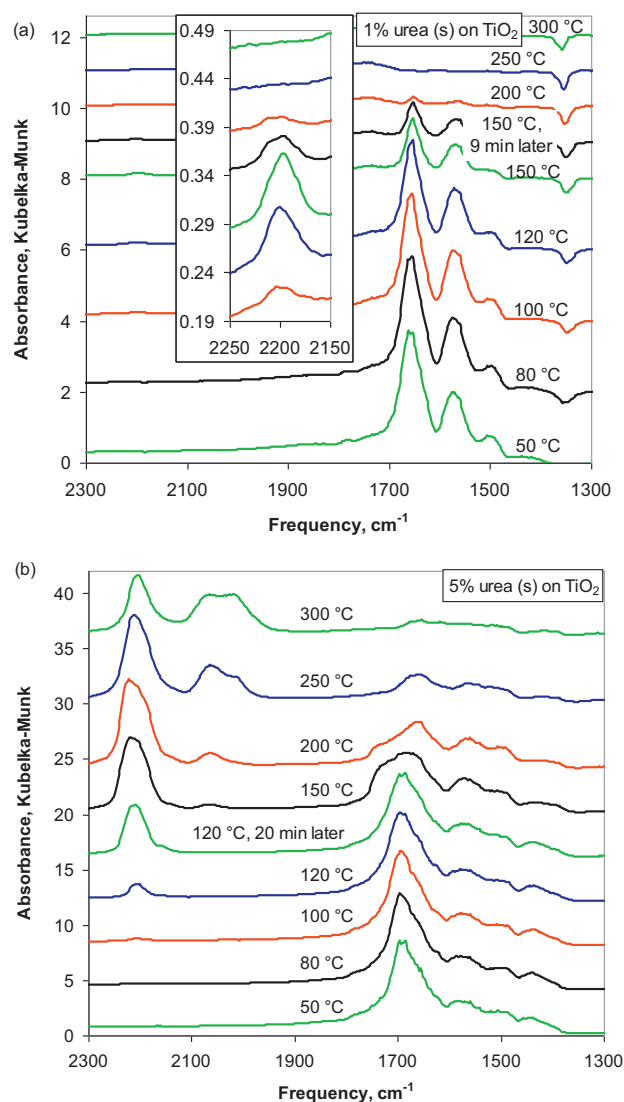
Notably, the peaks at  $1443\text{ cm}^{-1}$ ,  $1240\text{ cm}^{-1}$  and  $1198\text{ cm}^{-1}$  were not observed in the urea (aq) on  $\text{TiO}_2$  (Fig. 6a) or in the urea (s) on  $\text{TiO}_2$  (Fig. 3) spectra, which is tentatively explained by interaction between adsorbed molecules reduce their degree of freedom, which can suppress some theoretically observed vibrations like bending of  $\text{NH}$  groups. By contrast, only single molecules adsorbed onto the  $\text{TiO}_2$  surface with full degree of freedom were considered in our DFT calculations, which corresponds to a small coverage and an even distribution of urea at surface. Apparently, the urea was uniformly distributed in the urea (g) on  $\text{TiO}_2$  sample and its DRIFT spectrum could therefore be well represented by the DFT calculations (Fig. 6b).



**Fig. 6.** Comparison of DRIFT spectra with DFT-calculated frequencies and intensities (vertical lines) for the two adsorbed states shown in Fig. 5 (a) 1% urea (aq), (b) >1% urea (g).

### 3.5. Urea thermolysis followed by DRIFT spectroscopy

Fig. 7 shows DRIFT spectra measured during the decomposition of (a) 1% and (b) 5% urea on  $\text{TiO}_2$ . The urea was decomposed on the catalysts by increasing the temperature of the DRIFT cell stepwise (spectra were recorded at constant temperature). The spectra of the sample with the lower urea concentration of 1%, shown in Fig. 7a, remained substantially unchanged up to  $150^\circ\text{C}$ . At  $200^\circ\text{C}$ , most of the urea was decomposed. A close examination of the spectra (window with enlarged viewing in Fig. 7a) reveals a tiny peak that appeared at  $2202\text{ cm}^{-1}$  at  $100^\circ\text{C}$ , which was assigned to the asymmetric stretching vibrations of adsorbed  $\text{NCO}$  groups [5,22,23,25] produced by the catalytic thermolysis of urea into  $\text{HNCO}$  and  $\text{NH}_3$  [5,7,8]. The peak became more intense and shifted slightly to  $2200\text{ cm}^{-1}$  at  $120^\circ\text{C}$  and to  $2197\text{ cm}^{-1}$  at  $150^\circ\text{C}$ , where its intensity reached a maximum; however, the maximum-intensity peak was still significantly less intense than the peaks in the region of  $1700\text{--}1500\text{ cm}^{-1}$ . After 9 min at  $150^\circ\text{C}$ , the intensity of the  $\text{NCO}$  peak decreased again, and it disappeared completely at  $250^\circ\text{C}$ . Possibly, only a small amount of  $\text{NCO}$  could build up at the

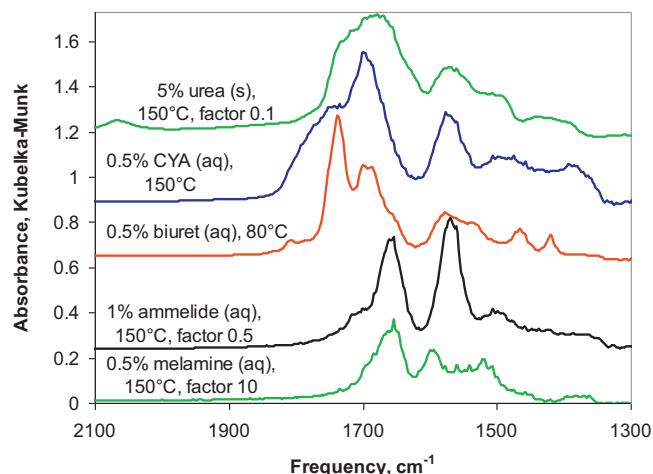


**Fig. 7.** DRIFT spectra measured during the decomposition of urea on  $\text{TiO}_2$ : (a) 1% urea and (b) 5% urea.

catalysts surface because it was steadily hydrolyzed with adsorbed water.

Fig. 7b shows DRIFT spectra measured during the decomposition of 5% urea on  $\text{TiO}_2$ . As previously mentioned in the discussion of Fig. 3, an increase in the urea concentration from 1% to 5% significantly changed the spectrum. We interpreted this behavior to be caused by a high surface coverage, which resulted in a spectrum with features of both bulk and adsorbed urea without simply being the sum of these two spectra. In analogy with the results reported by Larrubia et al. [5], heating the sample may desorb/decompose excessive urea so that a spectrum of adsorbed urea plus the decomposition products was observed at a certain temperature. Indeed, the three main peaks of adsorbed urea at  $1657\text{ cm}^{-1}$ ,  $1573\text{ cm}^{-1}$  and  $1501\text{ cm}^{-1}$  (Table 3) were observed in the spectrum of 5% urea on  $\text{TiO}_2$  at  $200^\circ\text{C}$ , with small shifts to  $1654\text{ cm}^{-1}$ ,  $1560\text{ cm}^{-1}$  and  $1506\text{ cm}^{-1}$  (Fig. 7b). Biuret probably was present as well, the pure biuret spectrum showed peaks at  $1653$ ,  $1570$  (most intensive),  $1506\text{ cm}^{-1}$  (Fig. 4b).

The decrease in the intensity of the largest peak at  $1695\text{ cm}^{-1}$  (the  $\text{NH}_2$  bending mode of bulk urea) upon heating was accompanied by the growth of several new peaks due to urea decomposition products and byproducts. Most importantly, isocyanate formation



**Fig. 8.** Comparison between “5% urea (s) on  $\text{TiO}_2$ ”, taken from Fig. 7, and the spectra of the urea decomposition byproducts cyanuric acid (CYA), biuret, ammeline and melamine (from top to bottom) on  $\text{TiO}_2$ .

was observed at the catalyst surface that showed peaks at  $2204\text{--}2222\text{ cm}^{-1}$ . The high intensity of the NCO band (Fig. 7b), which is in contrast to the low-intensity band obtained with the 1% urea (s) on  $\text{TiO}_2$  (Fig. 7a), was a consequence of the increased urea-to-water ratio. The use of 5% instead of 1% solid urea in the catalyst sample did not increase the amount of adsorbed water on the catalyst; hence, the major fraction of the HNCO could not be hydrolyzed.

At  $150^\circ\text{C}$ , a new band appeared at  $2066\text{ cm}^{-1}$  in the DRIFT spectrum (see Figs. 7b and 8), which we assigned, based on the work of Hauck et al. [22], to cyanamide adsorbed in the tautomeric and deprotonated form  $^-\text{N}=\text{C}=\text{NH}$ . Cyanamide is the monomer of melamine and can be formed by the disproportionation of HNCO into  $\text{CO}_2$  and cyanamide [26]. Cyanamide was also detected by HPLC (Table 1).

Furthermore, a shoulder at  $1740\text{ cm}^{-1}$  was observed in the spectra of 5% urea on  $\text{TiO}_2$  at  $150$  and  $200^\circ\text{C}$ , which we tentatively assigned to the  $\text{C}=\text{O}$  stretching mode of cyanuric acid (IUPAC name: 1,3,5-triazine-2,4,6-trione) in its trione tautomeric form. A DFT vibration analysis of gaseous cyanuric acid showed bands at  $1778\text{ cm}^{-1}$ ,  $1766\text{ cm}^{-1}$  and  $1764\text{ cm}^{-1}$  for this mode. The assignment of the shoulder at  $1740\text{ cm}^{-1}$  to cyanuric acid is supported by the spectrum of cyanuric acid on  $\text{TiO}_2$  shown in Fig. 8. Further, Fig. 8 suggests that ammeline (IUPAC name: 6-amino-1,3,5-triazine-2,4-diol) also contributed to the shoulder with its most intense peak at  $1737\text{ cm}^{-1}$  (Fig. 8).

At  $250^\circ\text{C}$ , the band at  $1740\text{ cm}^{-1}$  was no longer evident, which may be due to catalytic cyanuric acid de-polymerization into HNCO. This temperature is in fair agreement with the start of HNCO emissions between  $250$  and  $275^\circ\text{C}$  in a temperature programmed thermolysis experiment of cyanuric acid on  $\text{TiO}_2$  [9]. Another possible explanation for the disappearance of the cyanuric acid shoulder ( $1740\text{ cm}^{-1}$ ) at  $250^\circ\text{C}$  is the substitution of OH groups in cyanuric acid or ammeline with  $\text{NH}_3$ , which yields ammeline (IUPAC name: 4,6-diamino-1,3,5-triazine-2-ol) or melamine (IUPAC name: 1,3,5-triazine-2,4,6-triamine).

The disappearance of the cyanuric acid shoulder ( $1740\text{ cm}^{-1}$ ) at  $250^\circ\text{C}$  was accompanied by the growth of a new band at  $2019\text{ cm}^{-1}$ , which we could not assign.

#### 4. Conclusions

Gaseous urea was found, using HPLC analysis and DRIFT spectroscopy, to adsorb onto anatase  $\text{TiO}_2$  at  $100^\circ\text{C}$ . DFT calculations

suggested two different adsorbed states of deprotonated urea,  $\text{HN}^-\text{C}(\text{O})\text{NH}_2$ , to be present at the anatase (1 0 1) surface: in one state, urea bound at one Ti site with an adsorption energy of  $-0.26$  eV, and in the other state, urea was rotated and bound at two Ti sites with an adsorption energy of  $-0.28$  eV. Zwitterionic urea,  $\text{H}_2\text{NC}(\text{O}^+\text{H})\text{N}^-\text{H}$ , was also considered but abandoned, because the expected OH vibration was not observed in the DRIFT spectra. The confirmation of urea adsorption supports our previous conclusion that catalytic urea thermolysis is the rate-determining step in the overall urea hydrolysis reaction on anatase  $\text{TiO}_2$  to yield  $\text{NH}_3$  and  $\text{CO}_2$ , see refs [8,27].

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